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(12) **United States Patent**
Aduri et al.(10) **Patent No.:** **US 9,079,156 B2**(45) **Date of Patent:** **Jul. 14, 2015**(54) **IONIC FLUIDS**(75) Inventors: **Pavan Kumar Aduri**, Maharashtra (IN);
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H01M 10/0566 (2010.01)(52) **U.S. Cl.**CPC **B01J 27/138** (2013.01); **C07D 213/04**
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(2013.01); **C07F 3/06** (2013.01); **C07F 5/06**(2013.01); **C07F 7/2216** (2013.01); **C07F**
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(2013.01); **H01M 2300/0045** (2013.01)(58) **Field of Classification Search**CPC **C07F 1/04**; **C07F 1/08**; **C07F 3/06**;
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C07F 15/026; **C07D 213/04**; **H01B 1/122**;
B01J 27/138USPC **556/45**, **85**, **111**, **119**, **139**, **177**; **562/45**;
546/347; **502/168**

See application file for complete search history.

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mailed Dec. 1, 2012; ISA/CN.*Primary Examiner* — Porfirio Nazario Gonzalez(74) *Attorney, Agent, or Firm* — Harness, Dickey & Pierce,
P.L.C.(57) **ABSTRACT**A method for preparing an ionic compound by mixing at least
one compound of formula $C_xA_y \cdot zH_2O$ (1) with at least one
hydrogen donor and heating the mixture obtained is provided.
The said ionic compound remains in a physical state selected
from the group consisting of liquid and semisolid at a tem-
perature below 150° C., preferably below 125° C.**8 Claims, No Drawings**

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IONIC FLUIDS

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a U.S. National Stage of International Application No. PCT/IN2011/000422, filed on Jun. 22, 2011 and published in English as WO/2012/001703 on Jan. 5, 2012. This application claims the benefit of Indian Application No. 1899/MUM/2010, and filed on Jun. 29, 2010. The disclosures of the above applications are incorporated herein by reference.

FIELD OF THE INVENTION

This invention relates to ionic compounds and methods of preparation thereof.

BACKGROUND AND PRIOR ART

This invention relates to ionic compounds and methods for their preparation. In particular the invention relates to ionic compounds which are liquid or semi solid at a temperature below 150° C., preferably below 125° C.

There is a lot of interest in the field of ionic liquids in recent years and scientific publication and number of patent applications in this area are growing at very fast pace. Ionic systems, which are examples of viscous molten salts, have a number of interesting and useful properties, and have utility, for example, as highly polar solvents, co-solvents and catalyst in synthetic chemistry. They also have found to be useful in applications in various fields such as electrochemistry, synthesis of chemicals compounds, dyes, batteries, fuel cells, photovoltaic devices, electrodeposition processes, semiconductor cleaning, pyrolysis, gasification, in applications involving cellulose dissolution, for the electroplating of metals as described, for example in U.S. Pat. No. 6,573,405, U.S. Pat. No. 7,183,433, U.S. Pat. No. 7,196,221, US Patent Appl. No. 2005/0147889, U.S. Pat. No. 6,527,977, US Patent Appl. No. 2008/0307703, US Patent Appl. No. 2006/0183654, US Patent Appl. No. 2009/0247432.

Ionic liquids exhibits very low or no vapour pressure and thus, in contrast to many conventional molecular solvents and are produce virtually no vapours. They are therefore advantageous from a health, safety and environmental point of view.

U.S. Pat. No. 4,764,440 discloses low temperature molten compositions, formed by reacting, for example, trimethylphenylammonium chloride with aluminum trichloride. The resulting ionic compound has a low freezing point (around -75° C.), but suffers from the water sensitivity as EMIC- AlCl_3 , because of the presence of aluminum trichloride.

Other metal halides, in place of aluminum trichloride are reported, for example, U.S. Pat. No. 5,731,101 discloses the use of iron and zinc halides as the anion portion of an ionic liquid composition. The cation portion is formed by an amine hydrohalide salt, of the formula $\text{R}_5\text{N.H.X}$. This reference indicates however that the aluminum compounds are preferred, and indeed contains comparative examples which indicate that it is not possible to substitute SnCl_4 for aluminum trichloride. Furthermore, it does not suggest the use of quaternary ammonium compounds as cations.

In another disclosure, U.S. Pat. No. 5,892,124 liquid salts of the general formula Q^+A^- , wherein Q^+ represents quaternary ammonium or phosphonium, and A^- represents a vari-

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ous anions including tetrachloroaluminate, and trichlorozincate are disclosed. Diels-Alder reactions were suggested using the such compounds.

In another relevant disclosure, U.S. Pat. No. 6,573,405, ionic compound formed by the reaction of a quaternary ammonium compound of the formula $\text{R}^1\text{R}^2\text{R}^3\text{R}^4\text{N}^+\text{X}^-$ or a mixture of two or more thereof; with a halide of zinc, tin or iron, or a mixture of two or more thereof are disclosed. Preferably the choline chloride with zinc chloride ionic compound was suggested for applications in electrochemical, electrodeposition, electrochromics and dissolution of metal oxides, battery and Diels-Alder reactions. The examples of the invention teach us in which ionic liquid is prepared from a quaternary ammonium compound (Choline Chloride) and metal halide (zinc chloride) is common except for battery where iron halide was also used.

In yet another relevant disclosure, U.S. Pat. No. 7,183,433, ionic compound formed by the reaction of a quaternary ammonium compound of the formula $\text{R}^1\text{R}^2\text{R}^3\text{R}^4\text{N}^+\text{X}^-$ or a mixture of two or more thereof; with for example with urea.

Similarly, attempts were made to form ionic compounds of quaternary ammonium compound of the formula $\text{R}^1\text{R}^2\text{R}^3\text{R}^4\text{N}^+\text{X}^-$ and with specific hydrogen donors belonging to the families, such as carboxylic acids, amides, ethers, esters, aldehydes, ketones, alcohols, carbohydrates. Anions of quaternary ammonium compound of the formula $\text{R}^1\text{R}^2\text{R}^3\text{R}^4\text{N}^+\text{X}^-$ were chloride, nitrate and tetraborate and examples suggest that few ionic liquids were formed with the hydrogen donors, though many of them did not melt till 150° C. Effect of anion X^- was studied with symmetric amine salt by varying the anion. The example in which ionic compound made with urea suggests that asymmetric amine salts are preferred.

In yet another relevant disclosure, U.S. Pat. No. 7,196,221, ionic compound formed by the reaction of a quaternary ammonium compound of the formula $\text{R}^1\text{R}^2\text{R}^3\text{R}^4\text{N}^+\text{X}^-$ or a mixture of two or more thereof; with a hydrated metal salts (chlorides, nitrates, acetates, sulphate salts of) of chromium, calcium, magnesium, cobalt, zinc, copper, lithium, manganese, iron, nickel, cadmium, tin, lead, bismuth, lanthanum, cerium. Ionic liquids of other amine salts, tetraethylammonium chloride, triethylammonium chloride and benzyl trimethylammonium chloride with hydrated chromium chloride were also prepared. The examples teach us ionic compounds prepared in the current disclosure are used in applications of electrochemistry, chemicals synthesis and radical polymerization.

In yet another disclosure US Patent Application No. 2006/0183654, where ionic liquid formed by the reaction of imidazolium, pyridinium, pyrrolidinium, quaternary ammonium and phosphonium compounds with carboxylic acids, amides, sulfates, sulfonates and urea. The invention discloses the use of ionic liquids prepared from imidazolium, pyridinium, pyrrolidinium, quaternary ammonium and phosphonium as cation providing sources with carboxylic acids, amides and urea in semiconductor cleaning processes.

In yet another disclosure US Patent Application No. 2009/0247432, use of ionic liquid formed by the reaction of ammonium compound of the formula $\text{R}^1\text{R}^2\text{R}^3\text{R}^4\text{N}^+\text{Cl}^-$ and $\text{ClR}^1\text{R}^2\text{R}^3\text{R}^4\text{N}^+\text{Cl}^-$ and amides such as urea and carboxylic acids. The disclosure teaches us the use of ionic liquid in dissolving cellulose material from the subterranean region where cellulosic material was used as drilling and fracturing fluid.

DEFINITIONS

As used in the present specification, the following words and phrases are generally intended to have the meanings as set forth below, except to the extent that the context in which they are used indicates otherwise.

The phrase "ionic fluid" is used herein to refer to the solvate prepared whereby ionic compound is dissolved or ionic compound is formed in-situ by dissolving the mixture of salts in solvents.

The phrase "ionic fluid" is used herein to refer to an in situ formed solvated ionic compound in a solvent. The ionic fluid essentially comprises an entity formed by hydrogen bonding between a compound of Formula I and a hydrogen donor compound in the presence of a solvent.

Objects:

It is an object of the present invention to provide a process for preparation of ionic compounds that remain in a liquid or semisolid state at a temperature below 150° C.

It is another object of the present invention to provide a process for preparation of ionic fluids at room temperature.

SUMMARY OF INVENTION

In accordance with one aspect of the present invention, there is provided a process for preparation of an ionic compound that remains in a physical state selected from the group consisting of liquid and semisolid, at a temperature below 150° C., preferably below 125° C., comprising mixing at least one compound of Formula $C_XA_Y \cdot zH_2O$ (I)

wherein,

C is independently selected from the group consisting of Na, K, Li, Mg, Ca, Cr, Mn, Fe, Co, Mo, Ni, Cu, Zn, Cd, Sn, Pb, St, Bi, La, Ce, Al, Hg, Cs, Rb, Sr, V, Pd, Zr, Au, Pt, quaternary ammonium, imidazolium, phosphonium, and pyridinium, pyrrolidinium;

A is independently selected from the group consisting of Cl, Br, F, I, NO_3 , SO_4 , CH_3COO , $HCOO$ and C_2O_4 ; and

z is 0 to 20

with at least one hydrogen donor and heating the resulting mixture to obtain an ionic compound.

Typically, the hydrogen donor is at least one selected from the group consisting of toluene-4-sulphonic acid monohydrate, oxalic acid, maleic acid, citric acid and methane sulfonic acid.

Typically, the mixture is heated to up to 150° C.

In accordance with one embodiment, an ionic fluid is prepared from the ionic compound by dissolving the same in at least one solvent selected from the group consisting of carboxylic acids, amides, alcohols, amines, ketones (aldehydes), esters, alkyl halides, ethers, aromatics for example; methanol, ethanol, propan-1-ol, propan-2-ol, 1-butanol, isobutanol, 2-butanol, tert-butanol, dichloromethane, tetrahydrofuran, methyl acetate, ethyl acetate, acetone, dimethylformamide, acetonitrile, dimethyl sulfoxide, formic acid, acetic acid, methyl ethyl ketone, dimethyl carbonate, diethyl ketone, acetic anhydride, acetone, tert-butyl methyl ether, diethyl amine, diethylene glycol, N,N-dimethylacetamide, diethylene glycol dimethyl ether, ethylene glycol dimethyl ether, ethylene glycol, glycerin, hexamethylphosphor amide, hexamethylphosphorous triamide, isoamyl alcohol, 2-methoxyethanol, 2-methoxyethyl acetate, 1-methyl-2-pyrrolidinone, nitromethane, propanoic acid, pyridine, hydrogen fluoride, hydrogen chloride and water, to obtain a clear ionic fluid.

In accordance with another embodiment of the present invention an ionic fluid is prepared in situ by mixing the compound and the hydrogen donor in a solvent at a tempera-

ture in the range of 10° C. to 40° C. to obtain a clear ionic fluid that comprises an in-situ formed ionic compound.

Typically, the solvent is at least one selected from the group consisting of selected from the group consisting of carboxylic acids, amides, alcohols, amines, ketones (aldehydes), esters, alkyl halides, ethers, aromatics for example; methanol, ethanol, propan-1-ol, propan-2-ol, 1-butanol, isobutanol, 2-butanol, tert-butanol, dichloromethane, tetrahydrofuran, methyl acetate, ethyl acetate, acetone, dimethylformamide, acetonitrile, dimethyl sulfoxide, formic acid, acetic acid, methyl ethyl ketone, dimethyl carbonate, diethyl ketone, acetic anhydride, acetone, tert-butyl methyl ether, diethyl amine, diethylene glycol, N,N-dimethylacetamide, diethylene glycol dimethyl ether, ethylene glycol dimethyl ether, ethylene glycol, glycerin, hexamethylphosphor amide, hexamethylphosphorous triamide, isoamyl alcohol, 2-methoxyethanol, 2-methoxyethyl acetate, 1-methyl-2-pyrrolidinone, nitromethane, propanoic acid, pyridine, hydrogen fluoride, hydrogen chloride, and water.

In another aspect the present invention provides a clear ionic fluid as prepared by the process as mentioned herein above.

In still another aspect of the present invention, there is provided an ionic compound that remains in a physical state selected from the group consisting of liquid and semisolid, at a temperature at a temperature below 150° C., preferably below 125° C., said ionic compound being obtainable by the reaction of at least one salt of formula I wherein, C is Na, K, Li, Mg, Ca, Cr, Mn, Fe, Co, Mo, Ni, Cu, Zn, Cd, Sn, Pb, St, Bi, La, Ce, Al, Hg, Cs, Rb, Sr, V, Pd, Zr, Au, Pt, quaternary ammonium, imidazolium, phosphonium, pyridinium, pyrrolidinium;

A is Cl, Br, F, I, NO_3 , SO_4 , CH_3COO , $HCOO$ and C_2O_4 and z is 0 to 20

with at least one hydrogen donor selected from the group consisting of toluene-4-sulphonic acid monohydrate, oxalic acid, maleic acid, citric acid and methane sulfonic acid.

DESCRIPTION

The present invention provides a simple process to produce ionic compounds which remain in liquid or semi-solid state at a temperature below 150° C., preferably below 125° C.

The process for preparation of ionic compounds in accordance with the present invention comprises mixing at least one compound of Formula $C_XA_Y \cdot zH_2O$ (I)

wherein,

C is independently selected from the group consisting of Na, K, Li, Mg, Ca, Cr, Mn, Fe, Co, Mo, Ni, Cu, Zn, Cd, Sn, Pb, St, Bi, La, Ce, Al, Hg, Cs, Rb, Sr, V, Pd, Zr, Au, Pt, quaternary ammonium, imidazolium, phosphonium, and pyridinium, pyrrolidinium;

A is independently selected from the group consisting of Cl, Br, F, I, NO_3 , SO_4 , CH_3COO , $HCOO$ and C_2O_4 ; and

z is 0 to 20

with at least one hydrogen donor and heating the resulting mixture to obtain an ionic compound.

The hydrogen donors that are employed in the process accordance with this invention include toluene-4-sulphonic acid monohydrate, oxalic acid, maleic acid, citric acid and methane sulfonic acid.

Typically, the molar ratio of hydrogen bond donor to salt is in the range of 1:1 to 6:1.

Typically, the mixture is heated to a temperature up to about 100-150° C. to obtain the ionic compound.

The formation of ionic compound is the result of formation of hydrogen bond between the anion of the salt and hydrogen

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donor compound. As the salts mixture starts melting and turns as viscous liquid while heating, effervescence of acidic fumes are observed.

The hydrogen bond formed is relatively strong bond and it is retained even during heating. Acidic fumes are observed. In the wide range of temperatures the effervescence is observed and it depends on the salt that is forming ionic compound with hydrogen bond donor indicating the stability and strength of the hydrogen bond (Angew. Chem. Int. Ed., 2000, 39, 3772-3789, Ionic Liquids—New “Solutions” for Transition Metal Catalysis).

In a further aspect of the present invention there is provided a process for preparation of an ionic fluid. In accordance with one of the embodiments, the ionic fluid is prepared by dissolving the ionic compound obtained by the process of the present invention as described herein above in solvent at a temperature in the range of 10 to 40° C.

In accordance with another embodiment, the ionic fluid is prepared by mixing the ionic compound of the present invention with a solvent and heating to the same to a temperature up to 150° C.

In another embodiment, the hydrogen donor and the compound of Formula I are mixed in a solvent to obtain the ionic fluid of the present invention.

Typically, the solvents employed for preparation of the ionic fluid in accordance with the process of the present invention include carboxylic acids, amides, alcohols, amines, ketones (aldehydes), esters, alkyl halides, ethers, aromatics for example; methanol, ethanol, propan-1-ol, propan-2-ol, 1-butanol, isobutanol, 2-butanol, tert-butanol, dichloromethane, tetrahydrofuran, methyl acetate, ethyl acetate, acetone, dimethylformamide, acetonitrile, dimethyl sulfoxide, formic acid, acetic acid, methyl ethyl ketone, dimethyl carbonate, diethyl ketone, acetic anhydride, acetone, tert-butyl methyl ether, diethyl amine, diethylene glycol, N,N-dimethylacetamide, diethylene glycol dimethyl ether, ethylene glycol dimethyl ether, ethylene glycol, glycerin, hexamethylphosphor amide, hexamethylphosphorous triamide, isoamyl alcohol, 2-methoxyethanol, 2-methoxyethyl acetate, 1-methyl-2-pyrrolidinone, nitromethane, propanoic acid, pyridine, hydrogen fluoride, hydrogen chloride, and water.

The ionic compounds according to the present invention may be utilized for a wide variety of applications in chemical and electrochemical field. The particular applications include solubility of various chemicals such as fatty acids, greases, oils, metals, metal oxides and complexes, cellulose, various organic solvents. The ionic compounds also are used in extraction, surface modification.

Ionic compounds also found to be useful as inert media, as solvents, co-solvents, catalysts or as chemical reagents in the range of temperatures. In other applications, ionic compounds found useful as co-solvent and catalyst where aqueous and non-aqueous polar solvents may be employed. In other application, ionic compound was found to be useful in pure form or dissolved form in aqueous media or non-aqueous media as catalyst or co-solvent for chemical reactions.

Ionic compounds found to be useful as acid catalysts for chemical reactions in both liquid form and immobilized state.

Having described the invention in detail, it is obvious that one skilled in the art will be generally capable of selecting a suitable hydrogen donor for the purpose of the invention, based on the following specific examples herein.

The following examples further illustrate the present invention but are not to be construed as limiting the invention as defined in the claims appended hereto.

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The list of combination of hydrogen donor and salts given in Table 1 to 5 demonstrates that most but not all salts are capable of forming ionic compounds or ionic fluids with hydrogen bond donor compounds which are in principle capable of donating or sharing a hydrogen ion to a hydrogen bond.

TABLE 1

Compound I: Hydrogen Donor: Toluene-4-sulphonic acid monohydrate		
Ex-ample	Compound II: Salt	Melting Point ° C.
Chlorides		
1	Zinc Chloride	100 (Softens at 80)
2	Sodium Chloride	110 (Softens at 94)
3	Ferric Chloride	Not melted (softens at 90)
4	Cobaltous Chloride	Not melted (softens at 80)
5	Cuprous Chloride	115 (softens at 87)
6	Mangenuous Chloride	Not melted (softens at 75)
7	Nickel Chloride	Not melted (softens at 72)
8	Potassium Chloride	130 (softens at 90)
9	Calcium Chloride	Not melted
10	Stannous Chloride	Not melted (softens at 82)
11	Cesium Chloride	84 (softens at 74)
12	Magnesium Chloride	Not melted
13	Mercury Chloride	108
Fluorides		
14	Sodium Fluoride	(Not melted (softens at 120)
15	Calcium Fluoride	Not melted
16	Potassium Fluoride	(Not melted (softens at 125)
17	Magnesium Fluoride	(Not melted (softens at 105)
Sulphates		
18	Sodium Sulphate	120 (softens at 98)
19	Zinc Sulphate	(Not melted (softens at 104)
20	Aluminium Sulphate	(Not melted (softens at 85)
21	Ammonium Ferric Sulphate	90 (softens at 40)
22	Magnesium Sulphate	Not melted (softens at 25)
23	Calcium Sulphate	130 (softens at 65)
24	Ferrous Sulphate	(Not melted (softens at 65)
25	Cupric Sulphate	(Not melted (softens at 80)
26	Nickel Sulphate	Not melted (softens at 80)
27	Potassium Sulphate	142 (softens at 105)
Nitrates		
28	Sodium Nitrate	85
29	Aluminium Nitrate	70 (softens at 45)
30	Ammonium Nitrate	85
31	Potassium Nitrate	92
32	Nickel Nitrate	Not melted (softens at 25)
Bromides		
33	Potassium Bromide	105
34	Cobalt Bromide	Not melted (softens at 65)
35	Cetylpyridinium Bromide	90 (softens at 70)
36	Lithium Bromide	Not melted (softens at 130)
Acetates		
37	Sodium Acetate	Viscous Paste at 25*
38	Zinc Acetate	(Not melted (softens at 25)
39	Ammonium Acetate	Viscous Paste at 25*
40	Cobalt Acetate	(Not melted (softens at 65)
41	Manganese Acetate	(Not melted (softens at 65)
42	Lead Acetate	25

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TABLE 2

Compound I: Hydrogen Donor: Oxalic Acid		
Ex-ample	Compound II: Salt	Melting Point ° C.
Chlorides		
43	Zinc Chloride	(Not melted (softens at 25)
44	Sodium Chloride	100
45	Ferric Chloride	(Not melted (softens at 25)
46	Cobaltous Chloride	(Not melted (softens at 65)
47	Cuprous Chloride	(Not melted (softens at 105)
48	Mangenuous Chloride	95
49	Nickel Chloride	(Not melted (softens at 55)
50	Potassium Chloride	90
51	Calcium Chloride	(Not melted (softens at 95)
52	Stannous Chloride	95 (softens at 25)
53	Cesium Chloride	75 (softens at 63)
54	Magnesium Chloride	65 (softens at 25)
55	Mercury Chloride	115 (softens at 110)
Fluorides		
56	Sodium Fluoride	90
57	Calcium Fluoride	(Not melted (softens at 110)
58	Potassium Fluoride	(Not melted (softens at 75)
59	Magnesium Fluoride	(Not melted (softens at 120)
Sulphates		
60	Sodium Sulphate	104 (softens at 92)
61	Zinc Sulphate	25
62	Aluminium Sulphate	80 (softens at 65)
63	Ammonium Ferric Sulphate	25
64	Magnesium Sulphate	85
65	Calcium Sulphate	(Not melted (softens at 120)
66	Ferrous Sulphate	50 (softens at 35)
67	Cupric Sulphate	25
68	Nickel Sulphate	60 (softens at 50)
69	Potassium Sulphate	90 (softens at 80)
Nitrates		
70	Sodium Nitrate	85 (softens at 75)
71	Aluminium Nitrate	60 (softens at 45)
72	Ammonium Nitrate	70
73	Potassium Nitrate	80 (softens at 70)
74	Nickel Nitrate	70 (softens at 65)
Bromides		
75	Potassium Bromide	90
76	Cobalt Bromide	100 (softens at 55)
77	Cetylpyridinium Bromide	Not melted (softens at 90)
78	Lithium Bromide	90 (softens paste at 25)
Acetates		
79	Sodium Acetate	95 (softens at 25)
80	Zinc Acetate	78 (softens at 25)
81	Ammonium Acetate	Not melted (softens at 25)
82	Cobalt Acetate	Not melted (softens at 70)
83	Manganese Acetate	150 (softens at 85)
84	Lead Acetate	150 (softens at 60)

TABLE 3

Compound I: Hydrogen Donor: Maleic acid		
Ex-ample	Compound II: Salt	Melting Point ° C.
Chlorides		
85	Zinc Chloride	Not melted (softens at 109)
86	Sodium Chloride	145 (softens at 110)
87	Ferric Chloride	75 (softens at 25)
88	Cobaltous Chloride	90
89	Cuprous Chloride	150 (softens at 130)
90	Mangenuous Chloride	130
91	Nickel Chloride	120
92	Potassium Chloride	145

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TABLE 3-continued

Compound I: Hydrogen Donor: Maleic acid		
Ex-ample	Compound II: Salt	Melting Point ° C.
93	Calcium Chloride	125
94	Stannous Chloride	130 (softens at 90)
95	Magnesium Chloride	100
96	Mercury Chloride	150
Fluorides		
97	Sodium Fluoride	120
98	Calcium Fluoride	Not melted
99	Potassium Fluoride	125
100	Magnesium Fluoride	105
Sulphates		
101	Sodium Sulphate	150
102	Zinc Sulphate	100
103	Ammonium Ferric Sulphate	65
104	Magnesium Sulphate	115
105	Calcium Sulphate	115
106	Cupric Sulphate	130
107	Nickel Sulphate	140
108	Potassium Sulphate	147
Nitrates		
109	Sodium Nitrate	135
110	Aluminium Nitrate	95 (softens at 85)
111	Ammonium Nitrate	135 (softens at 85)
112	Potassium Nitrate	130
113	Nickel Nitrate	130 (softens at 65)
Bromides		
114	Potassium Bromide	150 (softens at 140)
115	Cobalt Bromide	120 (softens at 60)
116	Cetylpyridinium Bromide	105 (softens at 50)
117	Lithium Bromide	105 (softens paste at 70)
Acetates		
118	Sodium Acetate	80 (softens at 60)
119	Zinc Acetate	130
120	Ammonium Acetate	80 (softens at 60)
121	Cobalt Acetate	65
122	Manganese Acetate	65
123	Lead Acetate	65

TABLE 4

Compound I: Hydrogen Donor: Citric Acid		
Ex-ample	Compound II: Salt	Melting Point ° C.
Chlorides		
124	Zinc Chloride	80 (softens at 25)
125	Sodium Chloride	110 (softens at 65)
126	Ferric Chloride	65 (softens at 25)
127	Cobaltous Chloride	80
128	Cuprous Chloride	115 (softens at 105)
129	Mangenuous Chloride	75
130	Nickel Chloride	125 (softens at 65)
131	Potassium Chloride	105 (softens at 60)
132	Calcium Chloride	142 (softens at 69)
133	Stannous Chloride	110 (softens at 60)
134	Cesium Chloride	92 (softens at 40)
135	Magnesium Chloride	110
136	Mercury Chloride	150 (softens at 69)
Fluorides		
137	Sodium Fluoride	105
138	Calcium Fluoride	120
139	Potassium Fluoride	100
140	Magnesium Fluoride	70

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TABLE 4-continued

Compound I: Hydrogen Donor: Citric Acid		
Ex-ample	Compound II: Salt	Melting Point ° C.
Sulphates		
141	Sodium Sulphate	125 (softens at 75)
142	Zinc Sulphate	110 (softens at 85)
143	Aluminium Sulphate	125 (softens at 105)
144	Ammonium Ferric Sulphate	65 (softens at 53)
145	Magnesium Sulphate	110 (softens at 80)
146	Calcium Sulphate	120 (softens at 110)
147	Ferrous Sulphate	90 (softens at 73)
148	Cupric Sulphate	106 (softens at 85)
149	Nickel Sulphate	60 (softens at 50)
150	Potassium Sulphate	90
Nitrates		
151	Sodium Nitrate	125 (softens at 65)
152	Aluminium Nitrate	80 (softens at 60)
153	Ammonium Nitrate	102 (softens at 25)
154	Potassium Nitrate	95 (softens at 85)
155	Nickel Nitrate	95 (softens at 65)
Bromides		
156	Potassium Bromide	110 (softens at 65)
157	Cobalt Bromide	120 (softens at 70)
158	Cetylpyridinium Bromide	Not melted (softens at 85)
159	Lithium Bromide	135 (softens paste at 25)
Acetates		
160	Sodium Acetate	25
161	Zinc Acetate	70
162	Ammonium Acetate	100 (softens at 25)
163	Cobalt Acetate	85 (softens at 70)
164	Manganese Acetate	85 (softens at 70)
165	Lead Acetate	70

TABLE 5

Compound I: Hydrogen Donor: Methane sulfonic acid		
Ex-ample	Compound II: Salt	Melting Point ° C.
Chlorides		
166	Zinc Chloride	75 (softens at 25)
167	Sodium Chloride	105 (softens at 25)
168	Ferric Chloride	Not melted (softens at 25)
169	Cobaltous Chloride	105 (softens at 25)
170	Cuprous Chloride	25
171	Mangenuous Chloride	75 (softens at 25)
172	Nickel Chloride	120 (softens at 25)
173	Potassium Chloride	75 (softens at 25)
174	Calcium Chloride	Not melted (softens at 25)
175	Stannous Chloride	65 (softens at 25)
176	Magnesium Chloride	75 (softens at 25)
177	Mercury Chloride	75 (softens at 25)
Fluorides		
178	Sodium Fluoride	141 (softens at 25)
179	Calcium Fluoride	25
180	Potassium Fluoride	70 (softens at 25)
181	Magnesium Fluoride	120 (softens at 25)
Sulphates		
182	Sodium Sulphate	Not melted (softens at 25)
183	Zinc Sulphate	65 (softens at 25)
184	Ammonium Ferric Sulphate	25
185	Magnesium Sulphate	125 (softens at 25)

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TABLE 5-continued

Compound I: Hydrogen Donor: Methane sulfonic acid		
Ex-ample	Compound II: Salt	Melting Point ° C.
186	Calcium Sulphate	145 (softens at 25)
187	Cupric Sulphate	115 (softens at 25)
188	Nickel Sulphate	74 (softens at 25)
189	Potassium Sulphate	145 (softens at 25)
Nitrates		
190	Sodium Nitrate	75 (softens at 25)
191	Aluminium Nitrate	145 (softens at 25)
192	Ammonium Nitrate	25
193	Potassium Nitrate	110 (softens at 25)
194	Nickel Nitrate	130 (softens at 25)
Bromides		
195	Potassium Bromide	Not melted (softens at 25)
196	Cobalt Bromide	80 (softens at 25)
197	Cetylpyridinium Bromide	130 (softens at 25)
198	Lithium Bromide	70 (softens paste at 25)
Acetates		
199	Sodium Acetate	105 (softens at 25)
200	Zinc Acetate	Not melted (softens at 25)
201	Ammonium Acetate	70 (softens at 25)
202	Cobalt Acetate	110 (softens at 25)
203	Manganese Acetate	Not melted
204	Lead Acetate	105 (softens at 25)

Example 1

Toluene-4-sulphonic acid monohydrate, a hydrogen donor was mixed with Zinc chloride in molar ratio of 2:1, in a test tube and mixed with glass rod. A thick viscous paste was formed at room temperature. The viscous paste was heated slowly up to 150° C. and a milky white liquid was observed with effervescence. The ionic compound formed is cooled slowly and just below 95° C., crystal formation starts and on further cooling solid ionic compound was obtained. It demonstrates that hydrogen bond donor compounds which are in principle capable of donating a hydrogen ion to a hydrogen bond. By invention, the compounds which are forming most useful ionic compounds are the ones which melt at or below 150° C. by way of a reaction of a salt or a mixture of two or more thereof; with a hydrogen donor of the formula, or a mixture of two or thereof.

Examples 2-42

Toluene-4-sulphonic acid monohydrate, a hydrogen donor was mixed with a salt (compounds II), in molar ratio of 2:1, as given in Table 1 and having general formula $C_xA_y.zH_2O$ wherein C is cation, A is anion and z varies from 0 to n depends on hydration of the salt, in a test tube and mixed with glass rod to make uniform mixture. Procedure of example 1 is followed further to form ionic compound. In many but not all the cases, the liquid melt was observed below or near or at 120° C.

Examples 43-84

The procedure of examples 43-84 were followed example 1 except, Oxalic acid is a hydrogen donor instead of Toluene-4-sulphonic acid monohydrate (shown in table 2).

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Examples 85-123

The procedure of examples 85-123 were followed example 1 except, Maleic acid is a hydrogen donor instead of Toluene-4-sulphonic acid monohydrate (shown in table 3).

Examples 124-165

The procedure of examples 124-165 were followed example 1 except, Citric acid is a hydrogen donor instead of Toluene-4-sulphonic acid monohydrate (shown in table 4).

Examples 166-204

The procedure of examples 166-204 were followed example 1 except, Methane sulfonic acid is a hydrogen donor instead of Toluene-4-sulphonic acid monohydrate (shown in table 5).

Examples—205-408

The ionic compound formed in examples 1-204, was dissolved in suitable solvents for example water, methanol or DMF to form ionic fluid of respective ionic compound. In some cases but not all, ionic fluid is obtained by filtration of fine suspended solids.

Examples 409-612

Ionic fluid is formed by dissolving at least one of the Hydrogen Donor (compound I) with at least one of the salt (compound II) in suitable solvent for example water or methanol wherein they react to form hydrogen bond in the solvent to form ionic fluid. In many but not all the combinations, wherein solubility of compound I in combination with compound II is soluble or sparingly soluble, hydrogen bond was formed by process of dissolution and formation of ionic fluid. In some cases but not all, ionic fluid is obtained by the filtration of fine suspended solids.

Example—613

The ionic fluids prepared are used for carrying out the dehydration reaction at room temperature, for example 3,4 dimethyl benzaldehyde is reacted with sorbitol to form 3,4-dimethylbenzylidene sorbitol.

The ionic fluid prepared as given in example 1 is dissolved in methanol and 3,4 dimethyl benzaldehyde and sorbitol in 1:1 mole ratio are added to the ionic fluid and stirred for 5 hrs at room temperature. The reaction is stopped after 5 hrs and washed with ether followed by water. The 29% yield was obtained. The product was having 44% diacetal and 56% monoacetal.

Example—614

The ionic fluid prepared as given in example 1 is dissolved in methanol and 3,4 dimethyl benzaldehyde and sorbitol in 2:1 mole ratio are added to the ionic fluid and stirred for 8 hrs at room temperature. The reaction is stopped after 8 hrs and washed with ether followed by water. The 77% yield was obtained. The product was having 92% diacetal and 8% monoacetal.

Example—615

The procedure of example 614 is followed except, the reaction is carried out with the filtrate obtained from example

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614 and adding 3,4 dimethyl benzaldehyde and sorbitol in 2:1 mole ratio to the filtrate. The reaction is carried out for 8 hrs and washed with ether followed by water. The 88.5% yield was obtained. The product was having 94% diacetal and 6% monoacetal. This example illustrates the recyclability of ionic fluid for chemical reactions.

Example—616

The ionic fluid prepared as given in example 1 is dissolved in methanol and p-tolualdehyde and sorbitol in 1:1 mole ratio are added to the ionic fluid and stirred for 5 hrs at 26° C. The reaction is stopped after 8 hrs and washed with ether followed by water. The 30% yield was obtained. The product was having 37% diacetal and 63% monoacetal.

Example—617

The ionic fluid prepared as given in example 1, is dissolved in water and added to the ethyl acetate. The 5:1 water to ethyl acetate mole ratio was maintained. The reaction mixture is heated up to 50-55° C. and hydrolysis reaction is carried out for a period of 90 minutes. The reaction is stopped and product is analyzed through gas chromatograph and found the conversion of ethyl acetate to acetic acid and ethanol was in the range of 50-55%.

Example 618

The ionic fluid prepared as given in example 1, is dissolved in n-butanol and added to acetic acid. The 1:1 n-butanol to acetic acid mole ratio was maintained. The reaction is carried out at 26° C. and esterification reaction is carried out for a period of 30 minutes. The reaction is stopped and product is analyzed through gas chromatograph and found the conversion of acetic acid to butyl acetate was in the range of 65-70%.

Example 619

The ionic fluid prepared as given in example 1, carried out an alkylation reaction of olefins with benzene. 25 ml of C10-C11 Paraffin (containing 12% of olefins) and 25 ml of benzene were added to ionic fluid. The reaction is carried out at 80° C. and reaction is carried out for a period of 30 minutes. The reaction is stopped and product is analyzed through gas chromatograph and found the conversion of olefins to linear alkyl benzenes was in the range of 50%.

The numerical values given for various physical parameters, dimensions and quantities are only approximate values and it is envisaged that the values higher than the numerical value assigned to the physical parameters, dimensions and quantities fall within the scope of the invention and the claims unless there is a statement in the specification to the contrary.

While considerable emphasis has been placed herein on the specific features of the preferred embodiment, it will be appreciated that many additional features can be added and that many changes can be made in the preferred embodiment without departing from the principles of the invention. These and other changes in the preferred embodiment of the invention will be apparent to those skilled in the art from the disclosure herein, whereby it is to be distinctly understood that the foregoing descriptive matter is to be interpreted merely as illustrative of the invention and not as a limitation.

The invention claimed is:

1. A process for preparation of preparing an ionic compound that remains in a physical state selected from the group consisting of liquid and semisolid, at a temperature in the

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range of 35° C. to 150° C., the process comprising mixing at least one compound of Formula $C_xA_y \cdot zH_2O$ (I) with at least one hydrogen donor and heating the resulting mixture to obtain an ionic compound;

wherein C is independently selected from the group consisting of Na, K, Li, Mg, Ca, Cr, Mn, Fe, Co, Mo, Ni, Cu, Zn, Cd, Sn, Pb, St, Bi, La, Ce, Al, Hg, Cs, Rb, Sr, V, Pd, Zr, Au, Pt, quaternary ammonium, imidazolium, phosphonium, pyridinium, and pyrrolidinium;

A is independently selected from the group consisting of Cl, Br, F, I, NO_3 , SO_4 , CH_3COO , $HCOO$ and C_2O_4 ; and z is 0 to 20.

2. The process as claimed in claim 1, wherein the hydrogen donor is at least one selected from the group consisting of toluene-4-sulphonic acid monohydrate, oxalic acid, maleic acid, citric acid and methane sulfonic acid.

3. The process as claimed in claim 1, wherein the mixture is heated up to 150° C.

4. The process as claimed in claim 1, further comprising the method step of dissolving the ionic compound in at least one solvent selected from the group consisting of methanol, ethanol, propan-1-ol, propan-2-ol, 1-butanol, isobutanol, 2-butanol, tert-butanol, dichloromethane, tetrahydrofuran, methyl acetate, ethyl acetate, acetone, dimethylformamide, acetonitrile, dimethyl sulfoxide, formic acid, acetic acid, methyl ethyl ketone, dimethyl carbonate, diethyl ketone, acetic anhydride, tert-butyl methyl ether, diethyl amine, diethylene glycol, N,N-dimethylacetamide, diethylene glycol dimethyl ether, ethylene glycol dimethyl ether, ethylene glycol, glycerin, hexamethylphosphor amide, hexamethylphosphorous triamide, isoamyl alcohol, 2-methoxyethanol, 2-methoxyethyl acetate, 1-methyl-2-pyrrolidinone, nitromethane, propanoic acid, pyridine, hydrogen fluoride, hydrogen chloride and water, to obtain a clear ionic fluid.

5. An ionic compound prepared by the process as claimed in claim 1, that remains in a physical state selected from the group consisting of liquid and semisolid, at a temperature in the range of 35° C. to 150° C., said ionic compound being obtainable by the reaction of at least one salt of formula $C_xA_y \cdot zH_2O$ (I) with at least one hydrogen donor;

wherein C is independently selected from the group consisting of Na, K, Li, Mg, Ca, Cr, Mn, Fe, Co, Mo, Ni, Cu,

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Zn, Cd, Sn, Pb, St, Bi, La, Ce, Al, Hg, Cs, Rb, Sr, V, Pd, Zr, Au, Pt, quaternary ammonium, imidazolium, phosphonium, pyridinium, and pyrrolidinium;

A is Cl, Br, F, I, NO_3 , SO_4 , CH_3COO , $HCOO$ and C_2O_4 ; and

z is 0 to 20.

6. A process for preparing an ionic compound that remains in a physical state selected from the group consisting of liquid and semisolid, at a temperature in the range of 35° to 150° C., the process comprising mixing at least one compound of Formula $C_xA_y \cdot zH_2O$ (I) with at least one hydrogen donor in a solvent at a temperature in the range of 10° C. to 40° C. to obtain a clear ionic fluid that comprises an in-situ formed ionic compound;

wherein C is independently selected from the group consisting of Na, K, Li, Mg, Ca, Cr, Mn, Fe, Co, Mo, Ni, Cu, Zn, Cd, Sn, Pb, St, Bi, La, Ce, Al, Hg, Cs, Rb, Sr, V, Pd, Zr, Au, Pt, quaternary ammonium, imidazolium, phosphonium, pyridinium, and pyrrolidinium;

A is independently selected from the group consisting of Cl, Br, F, I, NO_3 , SO_4 , CH_3COO , $HCOO$ and C_2O_4 ; and z is 0 to 20.

7. The process as claimed in claim 6, wherein the solvent is at least one selected from the group consisting of methanol, ethanol, propan-1-ol, propan-2-ol, 1-butanol, isobutanol, 2-butanol, tert-butanol, dichloromethane, tetrahydrofuran, methyl acetate, ethyl acetate, acetone, dimethylformamide, acetonitrile, dimethyl sulfoxide, formic acid, acetic acid, methyl ethyl ketone, dimethyl carbonate, diethyl ketone, acetic anhydride, tert-butyl methyl ether, diethyl amine, diethylene glycol, N,N-dimethylacetamide, diethylene glycol dimethyl ether, ethylene glycol dimethyl ether, ethylene glycol, glycerin, hexamethylphosphor amide, hexamethylphosphorous triamide, isoamyl alcohol, 2-methoxyethanol, 2-methoxyethyl acetate, 1-methyl-2-pyrrolidinone, nitromethane, propanoic acid, pyridine, hydrogen fluoride, hydrogen chloride, and water.

8. A clear ionic fluid prepared by the process as claimed in claim 6.

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